Plasma Nitriding and Plasma Immersion Ion Implantation

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Outlines

- Introduction to nitriding
  - Objectives of the treatment
  - History of nitriding
  - Fundamentals of nitriding
- Plasma nitriding
  - Model of plasma nitriding
  - Process characteristic
  - Main technological parameters
  - Types of the processes
  - Advantages and limitations of the processes

Outlines

- Plasma Immersion Ion Implantation (PIII)
  – Concept of PIII
  – Types of the processes
  – Comparison with other techniques

- Examples of plasma nitriding applications
  – Low temperature nitriding of stainless steel
  – Plasma treatment of metallic biomaterials
  – Nitriding of sintered materials

Introduction to nitriding

Introduction to nitriding

NITRIDING it is a thermochemical method of diffusing of nascent nitrogen into the surface of materials to be treated. This diffusion process is based on the solubility of nitrogen in metal matrix.

- **Objectives of the nitriding**
  - to increase hardness and wear resistance
  - to increase fatigue resistance
  - to increase corrosion resistance

Introduction to nitriding

History

- 100 bc - China - first examples of carbonitrided elements

- 415 ac - India - iron made column covered with iron nitrides
- naturally nitrided

Introduction to nitriding

History

- GAS NITRIDING
- beginning of 20th century - Adolph Machelet - US - first work on nitriding - patent 1908
- Adolph Fry - Germany - patent 1921 - investigation on the role of alloying elements

- SALT BATH NITRIDING

Introduction to nitriding

History

- ION (PLASMA) NITRIDING
- Arthur Wehnelt and Bernhard Berghaus - glow discharge nitriding - 1932 - Klockner Ionen GmbH

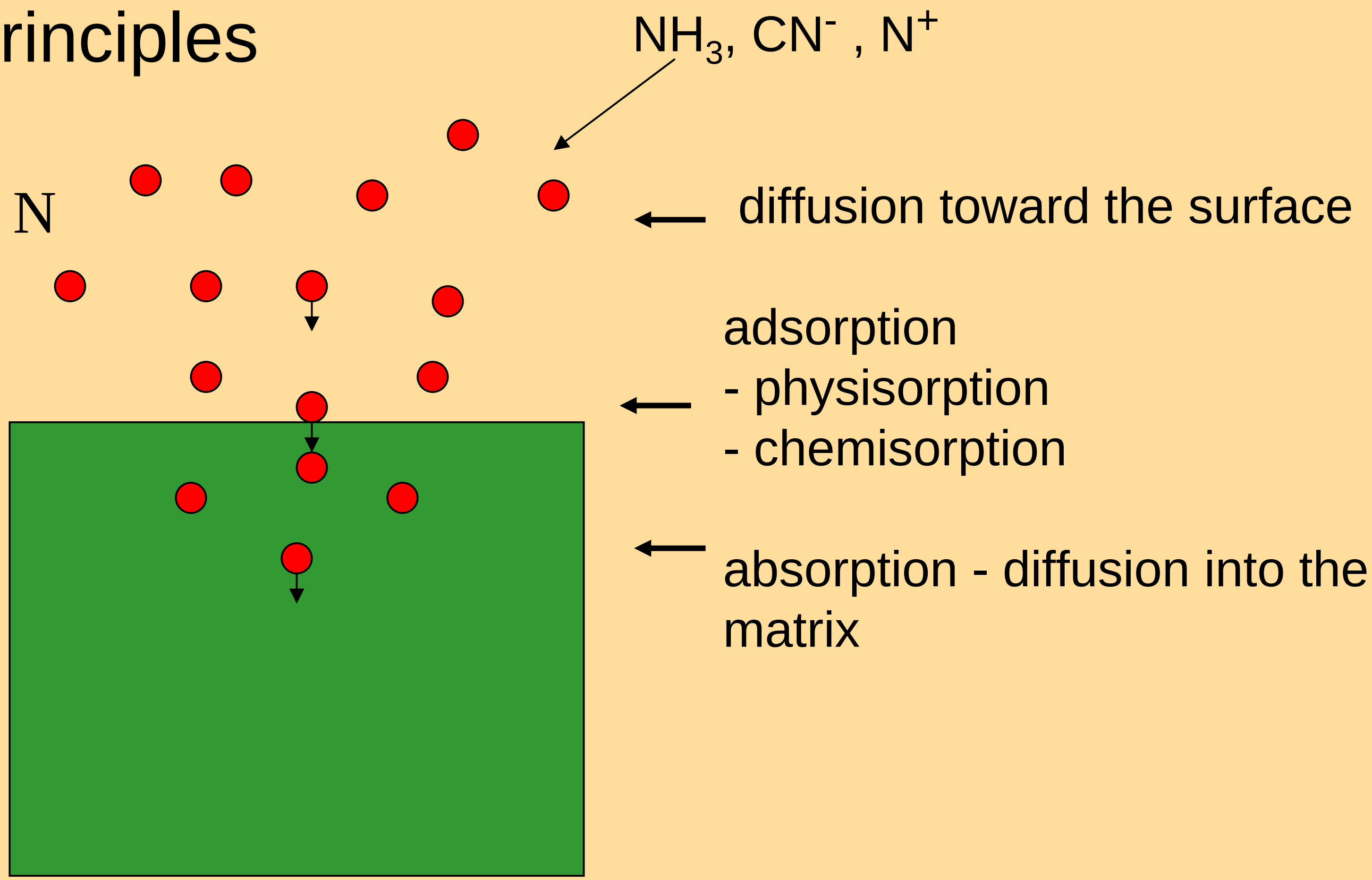
•1944-45 - nitriding of tank's barrels

•1970s - industrial acceptance of the process in Europe

•1990s - development of plasma immersion ion implantation

Introduction to nitriding

Principles



Introduction to nitriding

Principles

<u>Golden rules for diffusion treatment</u>

- an element has to be in atomic state (nascent)
- surface has to be able to adsorb the atom
- atom has to dissolve in the matrix

Introduction to nitriding

Principles

- **an element has to be in atomic state (nascent)**

Gas treatment - ammonia dissociation: NH_3=N + H_2

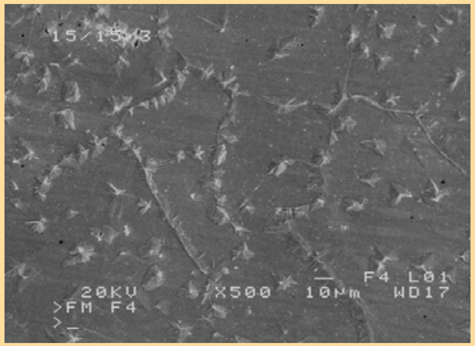
Salt bath treatment - decomposition of OCN^- group

Plasma treatment - nitrogen ions/atoms N^+

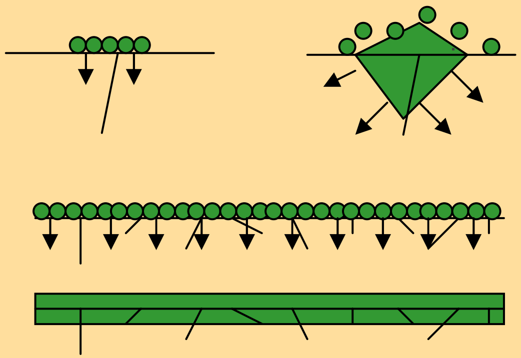
Introduction to nitriding

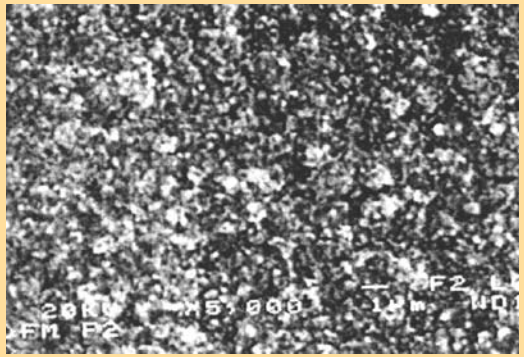
Principles

- **surface has to be able to adsorb the atoms**
- adsorption is an energy activated process - adsorption is promoted in the areas with increased surface energy - active centres
- active centres - irregularities on the surface (defects, roughness)



Polished surface & GN



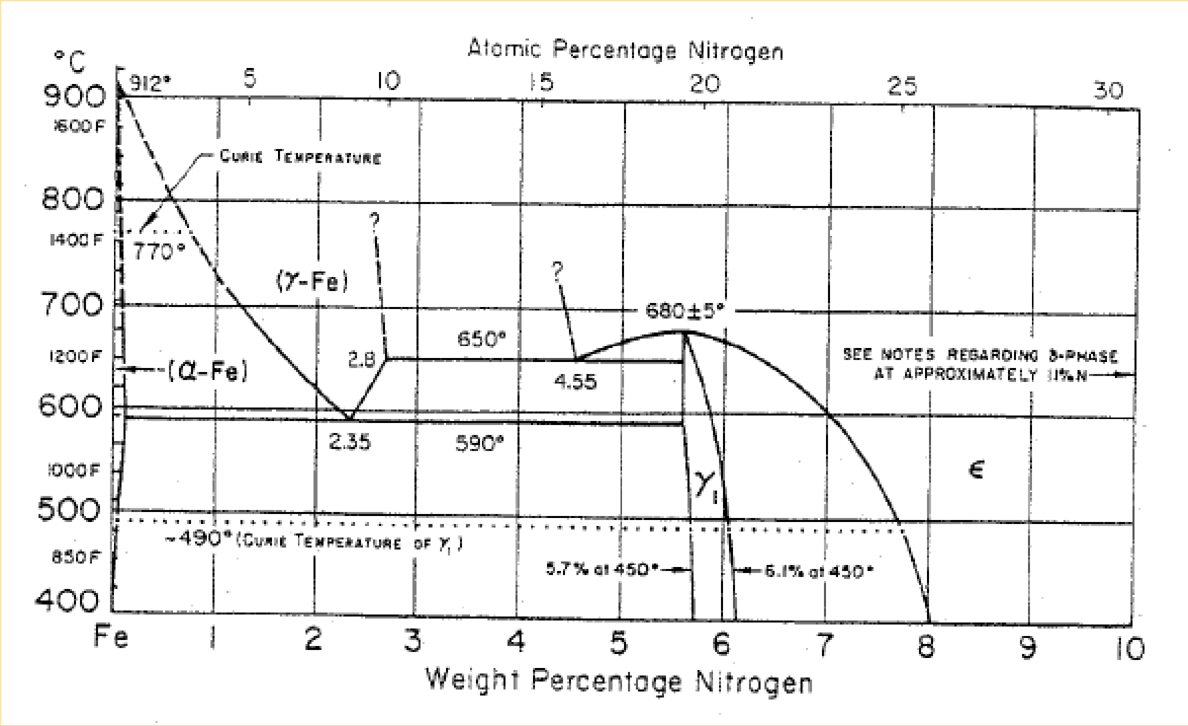


Pre-sputtered surface & GN

Introduction to nitriding

Principles

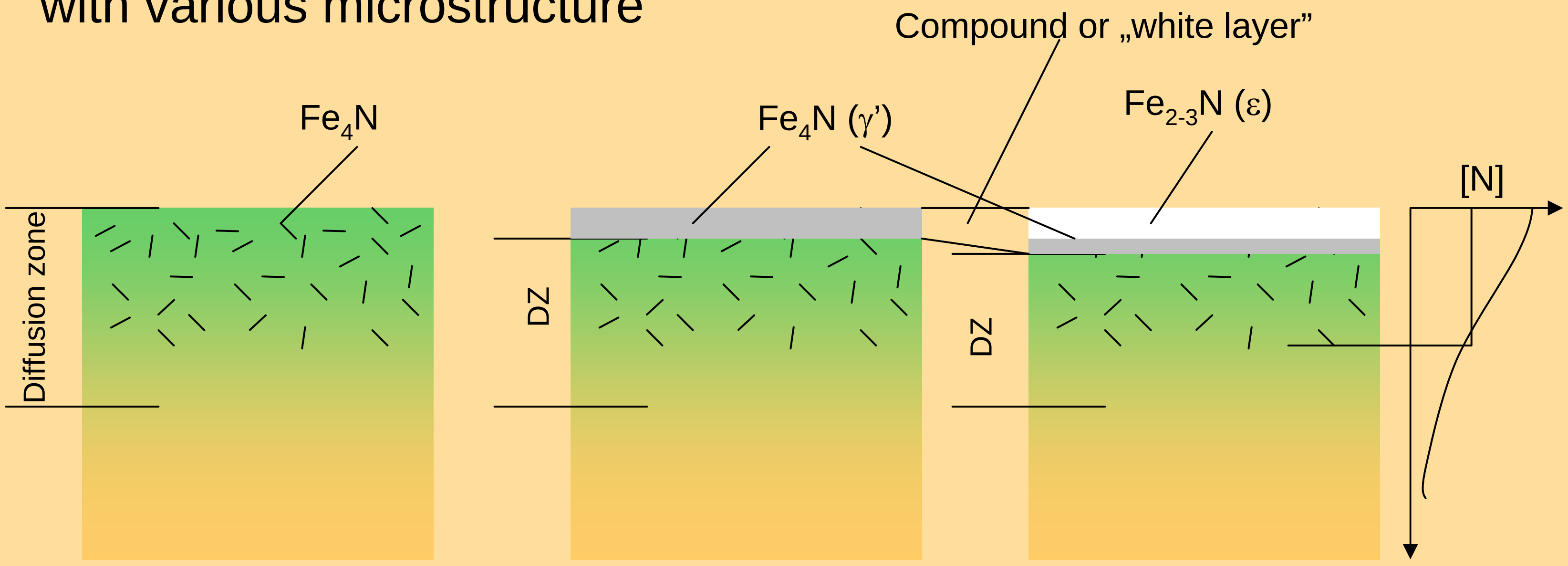
- **atoms has to dissolve in the matrix**



Introduction to nitriding

Microstructure of nitrided layer

depending on the nitrogen supply we can obtain nitrided layers with various microstructure

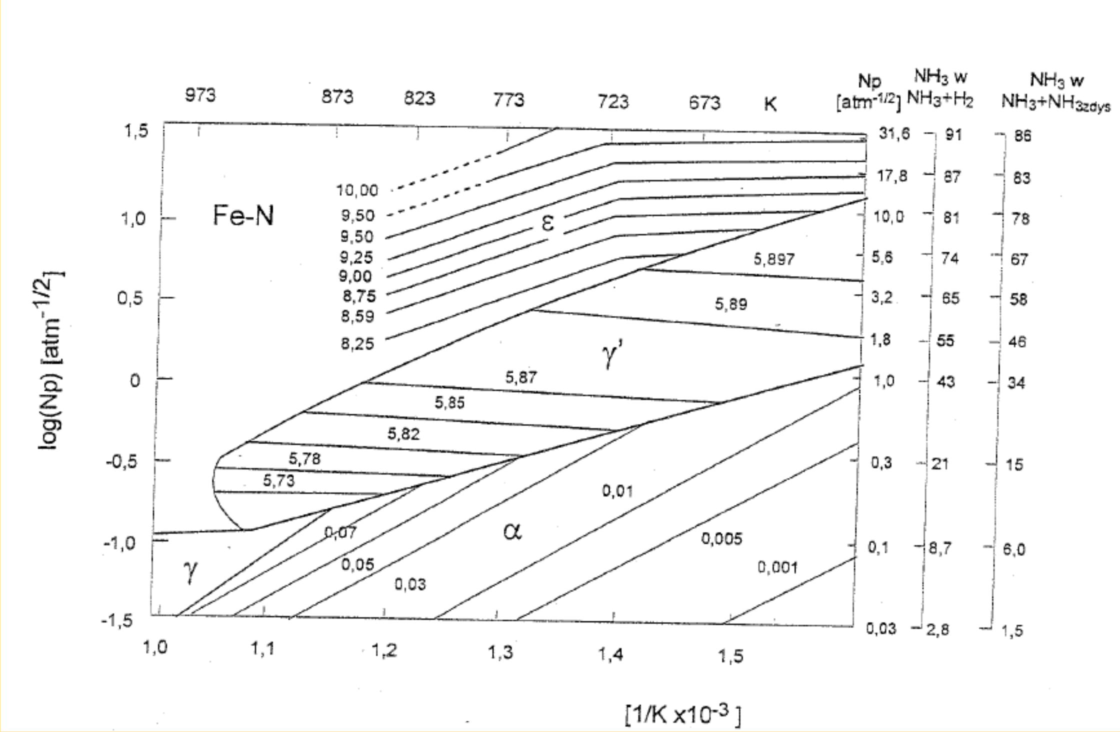


Introduction to nitriding

Microstructure of nitrided layer

$N_p = pNH_3/(pH_2)^{3/2}$

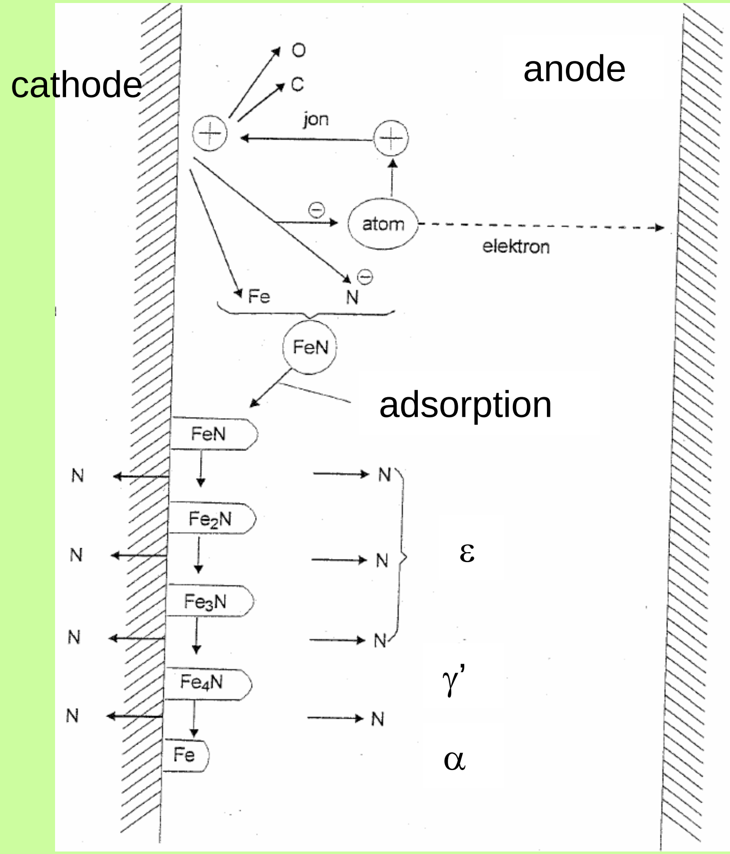
Lehrer's diagram



Plasma nitriding

Plasma nitriding

Model of plasma nitriding



Keller and Edenhofer - 1974

model of reactive sputtering

charged particles are responsible for the nitriding effect

Plasma nitriding

Model of plasma nitriding

70s

M. Hudis - NH^+ and NH^{2+} ions are responsible for nitrogen mass transfer

G.G. Tibbets - N^+ ions are the most important

80s

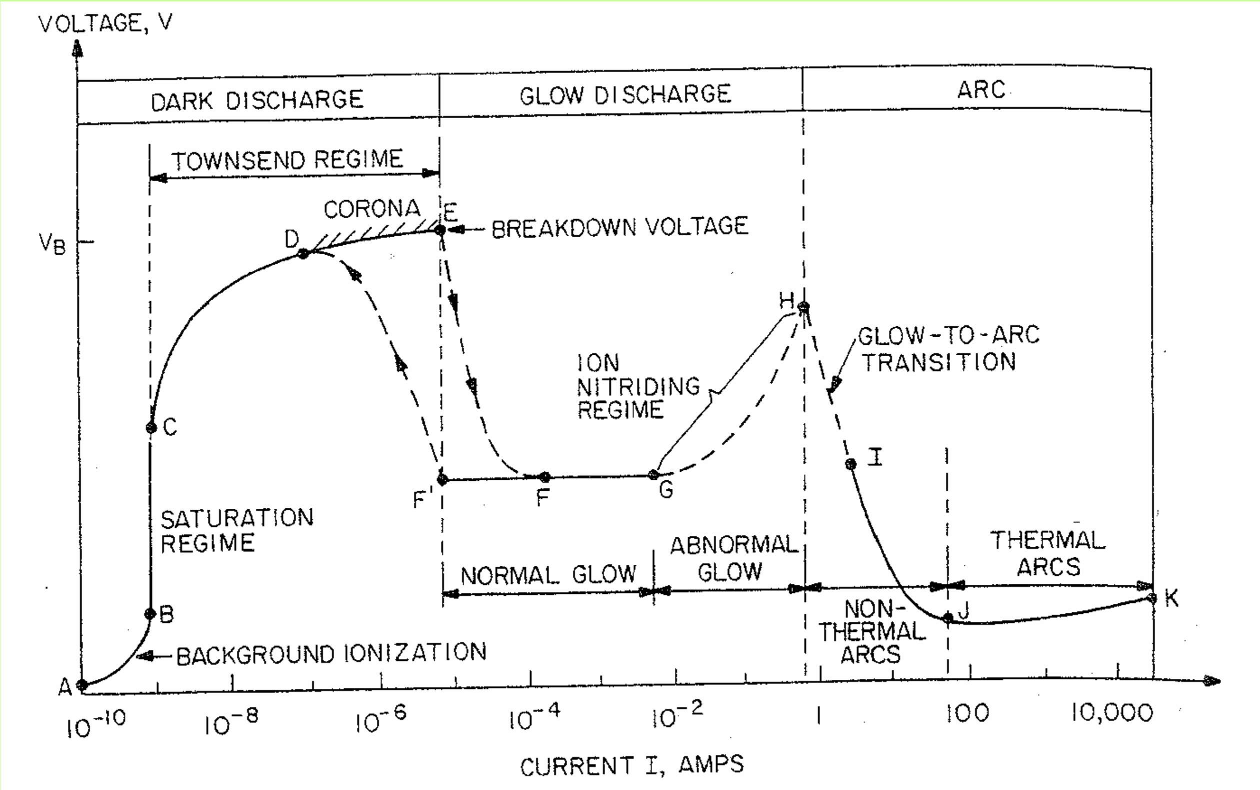
G.G. Marciniak - for heat transfer are responsible the excited neutral species and they are also responsible for mass transfer

90s

Ricard and Bougdira – confirmed that excited atoms and molecules are responsible for mass transfer

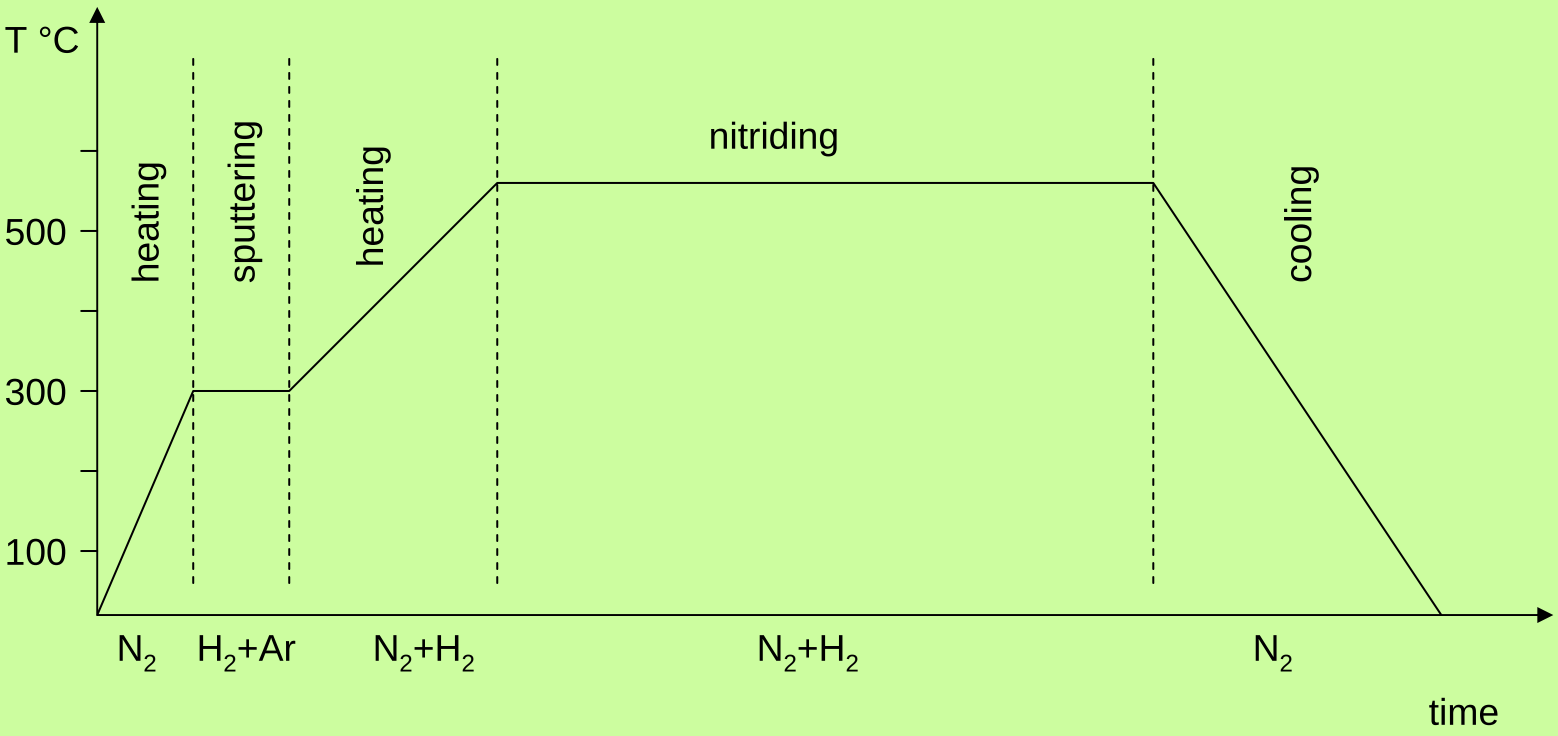
Plasma nitriding

Process characteristic



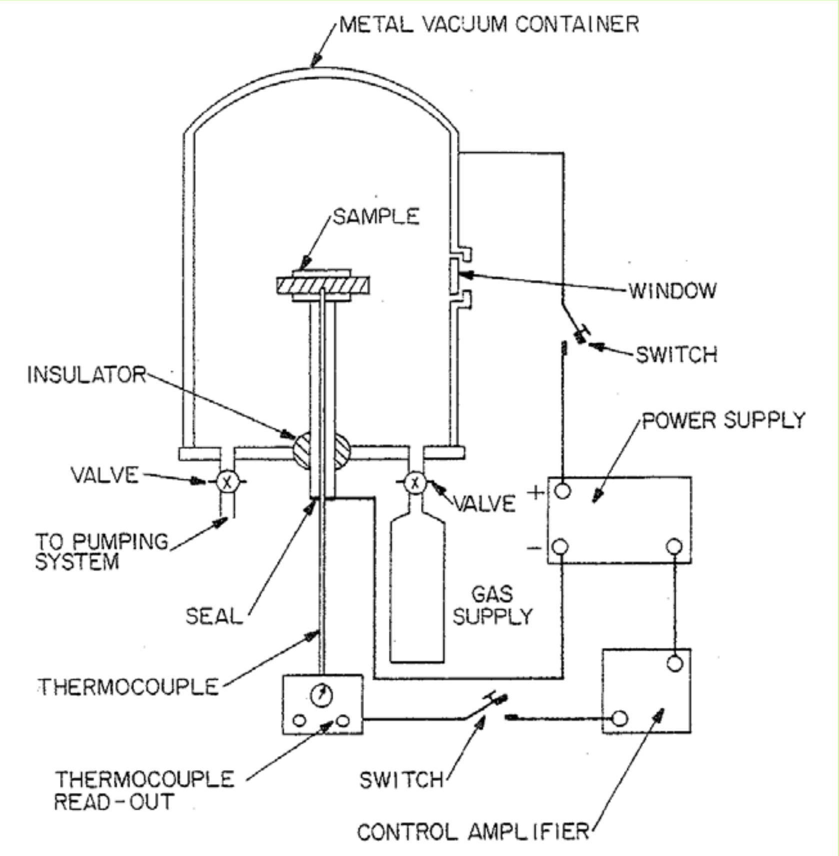
Plasma nitriding

Process characteristic



Plasma nitriding

Process characteristic



Plasma nitriding

Main technological parameters

Gas composition	$Fe_{2\text{-}3}N$ $H_2<N_2$ 1:3 or 1:4 Fe_4N $H_2>N_2$ 3:1 Compound layer free $H_2>>N_2$ 8:1 Other gases: NH_3, CH_4, only N_2 , Ar,
Time and temperature	
Voltage and current	
Gas pressure	

Plasma nitriding

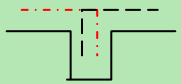
Main technological parameters

- Gas composition
- Time and temperature
- Voltage and current
- Gas pressure

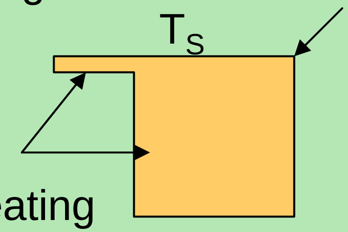
Determined by desired layer composition and thickness
$T = 530\text{-}570°C$, $t=3\text{-}40h$

Main problem - temperature uniformity

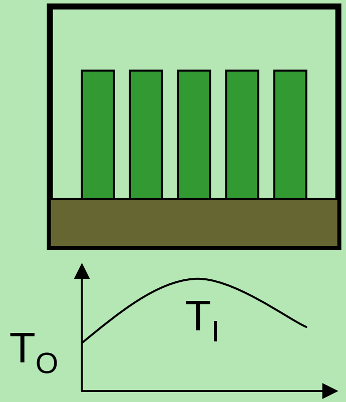
Hollow cathode effect



Edge effect



complex shape



Plasma nitriding

Main technological parameters

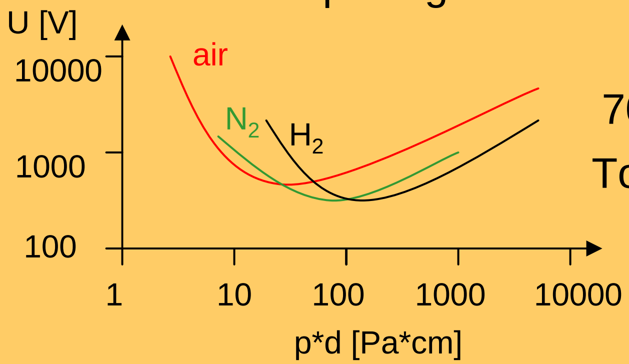
Gas composition

Time and temperature

Voltage and current

Gas pressure

Determined by type and pressure of the gas, electrode spacing and workpiece material



700V - kilovolts

Too high voltage - risk of arcing

Current affects workpiece temperature

with auxiliary heating → 0.2-5 mA/cm^2 ← without

Plasma nitriding

Main technological parameters

Gas composition

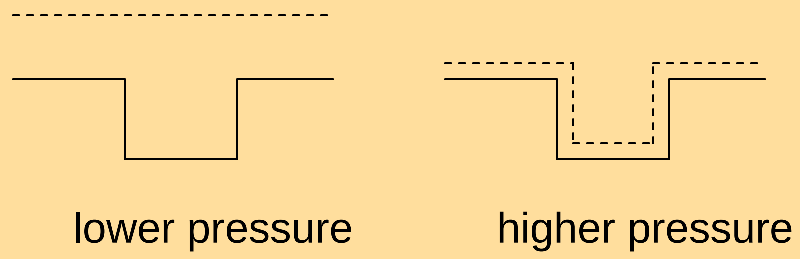
Time and temperature

Voltage and current

Gas pressure

Typical working pressure

1-10 Tr



Plasma nitriding

Types of processes

DC process – principal limitations

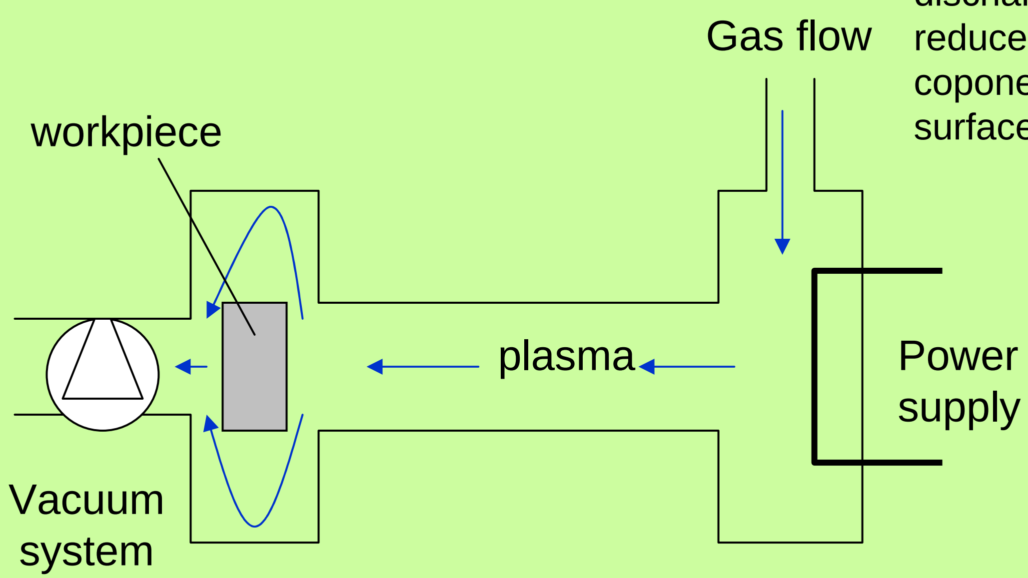
- large temperature differences in a load
- small loading density
- high energy consumption
- high risk of arcing

Plasma nitriding

Types of processes

Post discharged nitriding

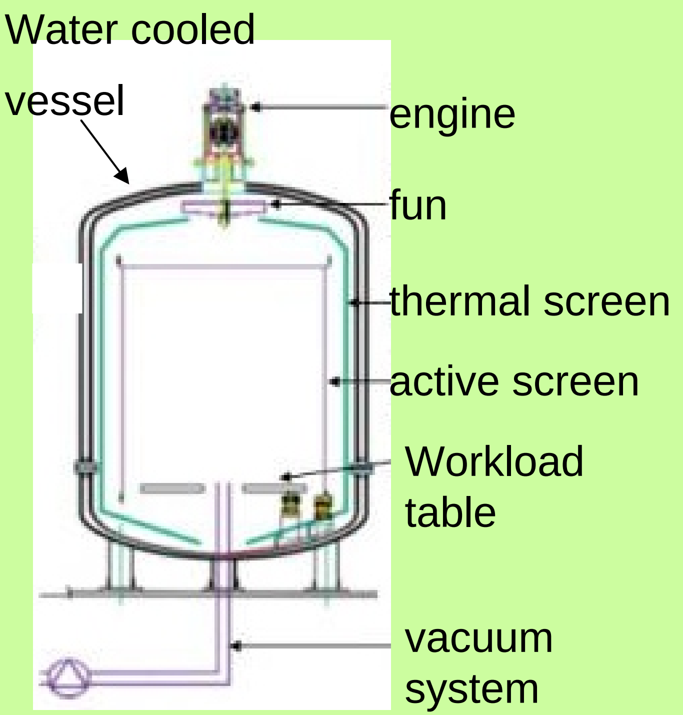
- uniform distribution of the plasma in heavily loaded chamber - very difficult,
- short life-span of glow discharged plasma - reduced number of active coponents reaching the surface

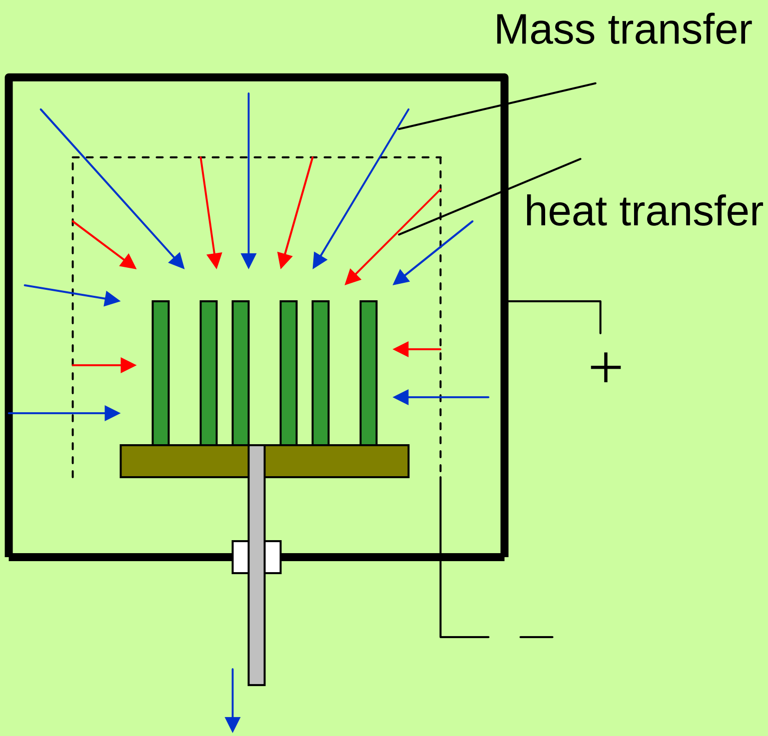


Plasma nitriding

Types of processes

Cage plasma nitriding (Active screen nitriding)

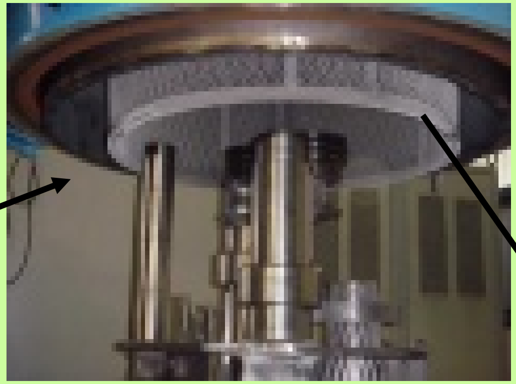


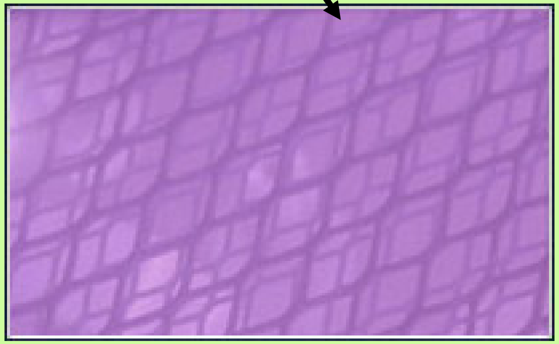


Plasma nitriding

Types of processes

Cage plasma nitriding (Active screen nitriding)

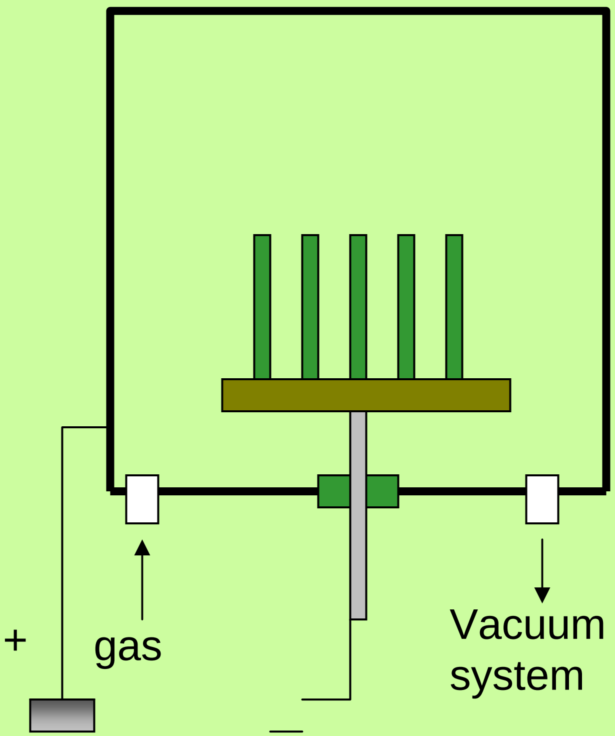


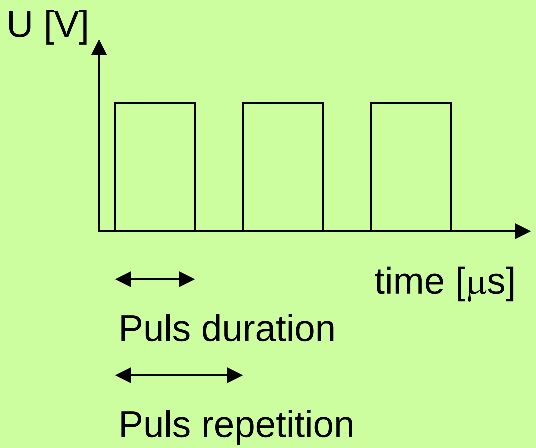


Plasma nitriding

Types of processes

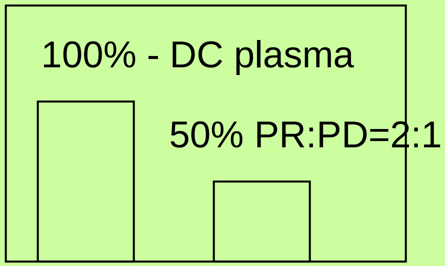
Pulsed Plasma Nitriding





Puls duration time: 50-100 μs

Puls repetition time: 100-300 μs



Plasma nitriding

ASN and PPN versus DC plasma nitriding

AS and PPN

- Good energy efficiency
- good homogenity of temperature distribution
- treatment result weakly dependent on shape and density of the load
- arcing probability very limited
- posiblity of treatment of the holes and pipes
- fast external heating

DC plasma nitriding

- Energy surplus
- high temperature gradient
- niriding layer distribution strongly depends on size and load density
- big risk of arcing
- difficulties in hole and pipes treatment
- heating by plasma

Plasma nitriding

Plasma nitriding in comparison to other methods

Advantages:
- clean technology
- layers with designed composition
- efficient use of gas end electrical energy
- easy automation of the process
- selective nitriding by simple masking techniques
- reduced nitriding time
- very good reproducibility and close tolerances
- no restrictions regarding the materials to be treated
- smaller roughness and internal stresses
- compact and dense compound layer

Disadvantages:
- inhomogeneous plasma distribution
- limited temperature control
- expensive equipment

Plasma Immersion Ion Implantation

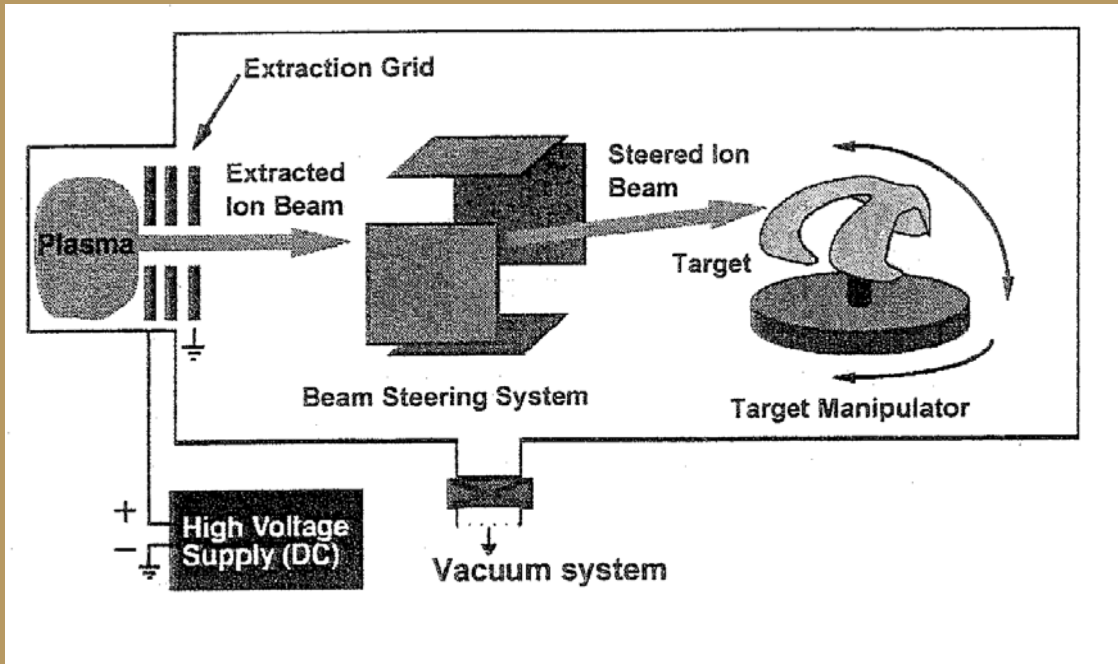
Plasma Immersion Ion Implantation (PIII)

Concept of PIII

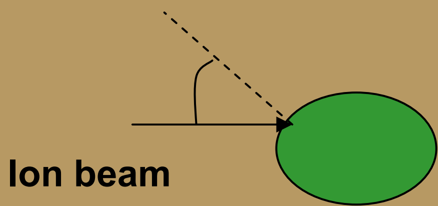
Ion energies - 20-600keV

implantation dose: 10^{14}-10^{18} ions/cm^2

Conventional beamline ion implantation



- **line-of-sight technique**
- **cooling necessary**
- **workpiece manipulation**
- **max. retained dose depends on angle of incidence**

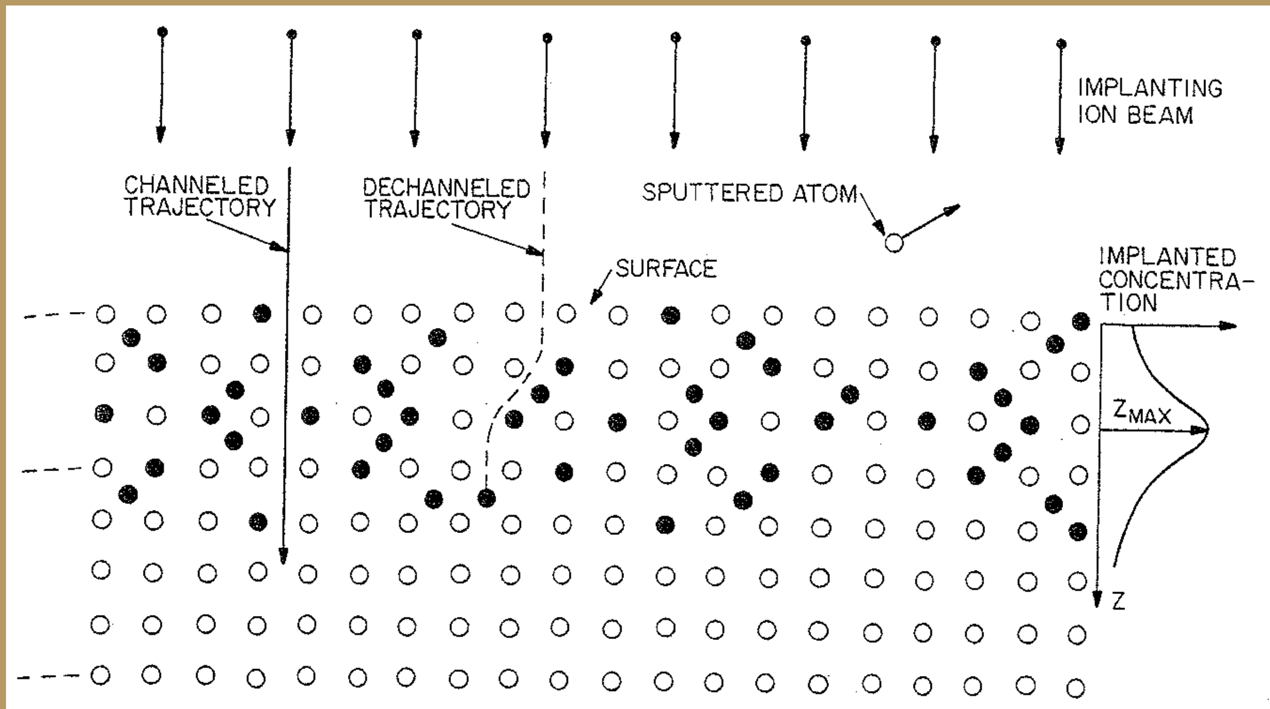


Plasma Immersion Ion Implantation (PIII)

Concept of PIII

Mechanisms of ion implantation

Implantation depth - up to 100nm

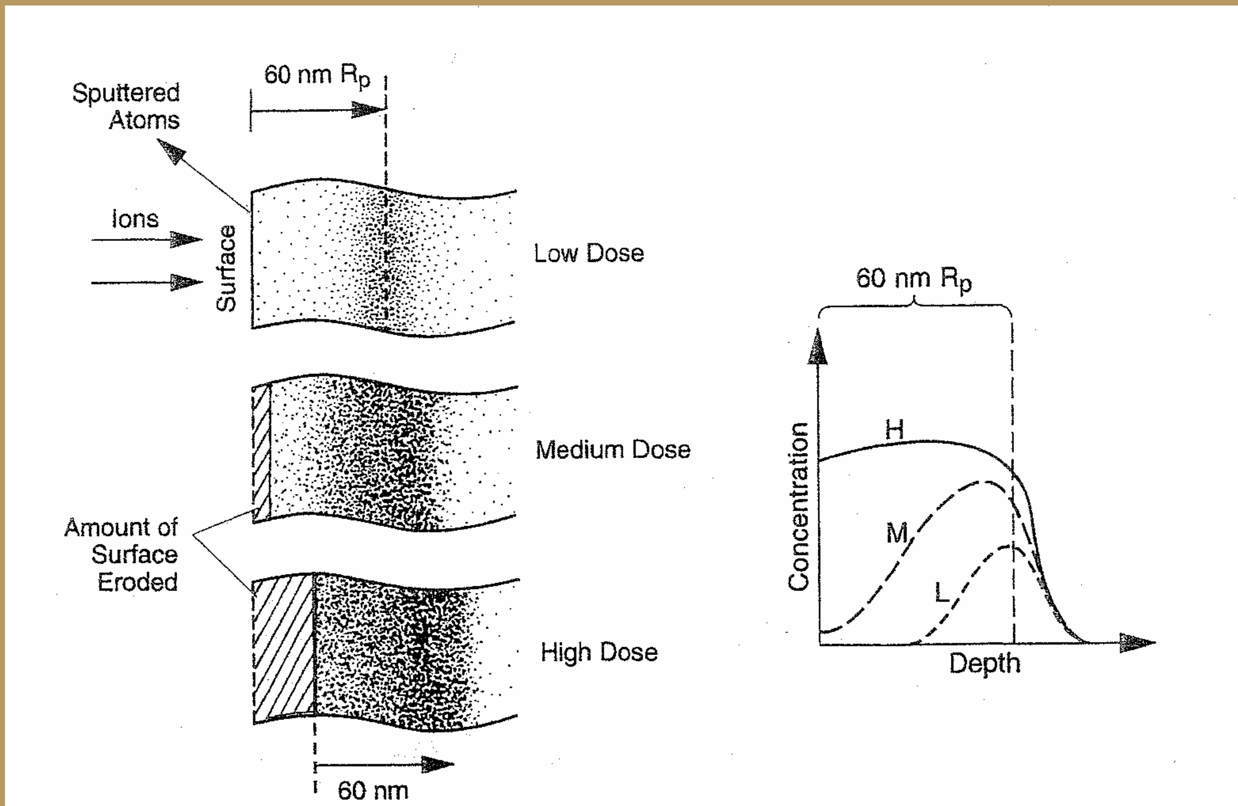


Plasma Immersion Ion Implantation (PIII)

Concept of PIII

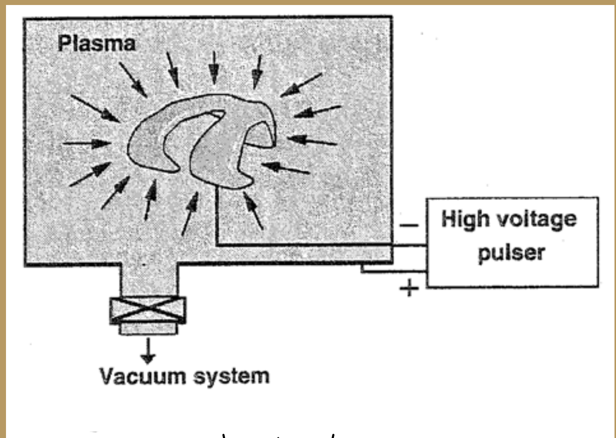
Profile of ion implantation

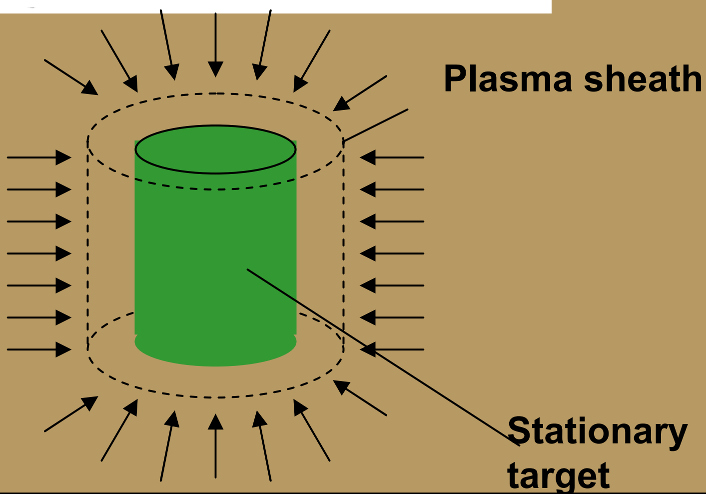
- **Surface sputtering**
- **radiation-enhanced diffusion**

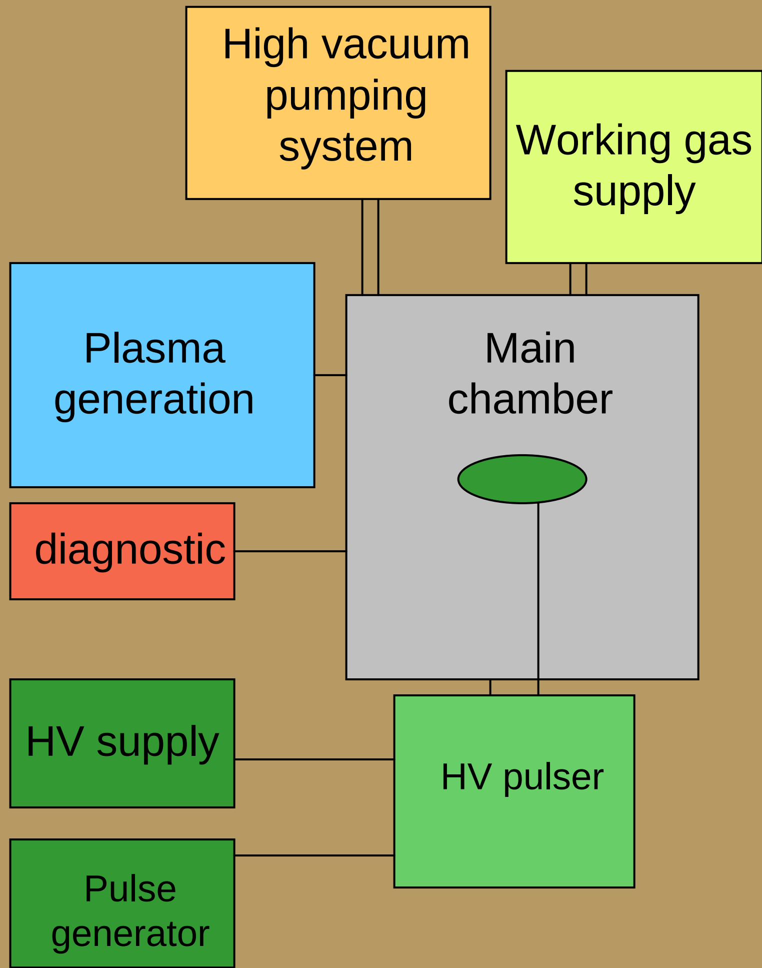


Plasma Immersion Ion Implantation (PIII)

Concept of PIII







Plasma Immersion Ion Implantation (PIII)

Comparison with PBII

advantages

- non-line-of-sight
- time independent of surface area
- low-temperature process
- easy combination with deposition
- high ion beam flux at low ion energy

disadvantages

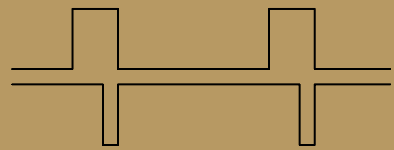
- no charge-to-mass separation
- inhomogeneous energy distribution
- for homogenous implantation:
  min. feature size>sheath with
- secondary electrons limits efficiency
  and generates X-rays
- difficult accurate in situ dose monitoring

Plasma Immersion Ion Implantation (PIII)

Hybrid treatment

Arc pulse

Substrate bias pulse



PIII + deposition → MePIIID

→ Active gas MePIIID

\+

diffusion → annealing

→ Plasma treatment

Literature

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